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(54) Title: STABILIZATION OF MARINE OILS**(57) Abstract**

Fully or partially refined marine oil is stabilized by treatment with silica and the incorporation of a lecithin, ascorbyl palmitate and a tocopherol in the thus-treated oil.

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Stabilization of Marine Oils

The present invention relates to the stabilization of marine oils, more particularly of fully or partially refined marine oils.

Marine oils have attracted substantial interest as a source of
5 long-chain polyunsaturated fatty acids, particularly eicosapentaenoic acid (EPA), docosapentaenoic acid (DPA) and docosaheptaenoic acid (DHA), which are considered to be of dietary significance. These fatty acids contain 5 or 6 double bonds, which render them prone to atmospheric oxidation. It is believed that the peroxides produced in
10 this oxidation break down to secondary oxidation products, which exhibit a pronounced taste and smell of fish.

It has been known for a long time that refined marine oil is initially free from a taste and smell of fish, but that reversion through
15 oxidation occurs rapidly. Attempts have been made to stabilize the oil by the addition of α -tocopherol or mixed tocopherols at a level of 0.1%, but this has resulted only in a short term improvement in stability, i.e. a few days. Stabilization with tetrabutylhydroquinone has also been proposed, but this is of very restricted application
20 having regard to the extremely bitter taste of this compound.

There has accordingly been a need for a process by means of which such marine oil can be stabilized over a long period in a simple and economical manner.

25

It has now surprisingly been found in accordance with the present invention that fully or partially refined marine oil can be stabilized over a longer period than hitherto, particularly over several months, by treating the oil with silica and incorporating a lecithin,
30 ascorbyl palmitate and a tocopherol in the thus-treated oil.

The present invention is based on the foregoing finding and is accordingly concerned with a process for the stabilization of fully or partially refined marine oil, which process comprises treating said oil
35 with silica and incorporating a lecithin, ascorbyl palmitate and a tocopherol in the thus-treated oil.

The partially purified marine oil used in the present invention is one which has been neutralized and bleached in a conventional manner and the fully refined marine oil, also used in the present invention, is one which has been subjected to the additional step of deodorization, likewise in a conventional manner. It is preferred to use a fully refined marine oil in the present invention. The oil can be, for example, herring oil, anchovy oil, sardine oil, menhaden oil, pilchard oil, shark oil, hake oil etc. or a blend of one or more of these oils.

The silica used in the present invention can be any conventional silica such as, for example, those available as Trisyl and Trisyl 300 (Grace), Britesorb (Akzo) or SD959, SD1027 and Sorbsil C60 (Crosfield). It is preferred to use a silica which is dried or substantially freed from water before or during the process, i.e. which preferably has a water content of up to about 2%, preferably up to about 1%. The drying of the silica can be achieved, for example, by heating at about 100°C for about 3 hours. Alternatively, the silica can be dried in heated oil under a vacuum or by azeotropic distillation.

The treatment of the oil with silica can suitably be carried out in one embodiment by contacting the oil with the silica in a silica-filled column or stirred reactor vessel or a combination thereof. Batch, semi-batch or continuous operation is feasible. In a preferred aspect, silica having a surface area of more than 500 m² per gram is used. It is preferred to carry out this treatment at about room temperature, although lower or, especially, higher temperatures may also be used if desired. Further, it is preferred to perform this embodiment under the atmosphere of an inert gas, especially nitrogen. The contact time between the oil and the silica can be varied within wide limits and can be a few seconds to several days. In this connection, the flow rate at which the oil passes through the silica in a column procedure will depend on factors such as the type and particle size of the chosen silica, the dimensions of the column and the like.

In another embodiment, an oil/solvent miscella is passed through a silica column. The solvent is preferably a food grade

approved apolar solvent, preferably a hydrocarbon and especially hexane. This embodiment can be carried out e.g. by dissolving the oil in the solvent to provide a solution containing about 20-60%, preferably 33%, oil by weight, passing the solution through silica in a column or stirred reactor vessel or a combination thereof using a ratio of miscella to silica of 20:1 to 5:1, preferably 15:1, (wt./wt.), filtering and then removing the solvent by distillation. Here again, the contact time between the oil and the silica can be varied within wide limits and can be a few seconds to several days.

10

The treatment with silica described hereinbefore can also be carried out in the presence of carbon. The carbon which is used is preferably dried or substantially freed from water before or during the process and, furthermore, preferably has a surface area of more than 1100 m² per gram. Examples of suitable carbons are those available as Norit, e.g. Norit CA1, and similar activated carbons.

15

In the next stage of the process, a lecithin, ascorbyl palmitate and a tocopherol are incorporated in the silica-treated oil.

20

Any food-grade or cosmetic-grade lecithin can be used in the present invention. It is, however, preferred to use a solid and/or liquid food-grade lecithin which is commercially available. An example of such a lecithin is Epikuron 100G (Lucas Meyer, D-2000 Hamburg, Germany).

25

Likewise, any tocopherol can be used in the present invention, with examples of such tocopherols being α -tocopherol, γ -tocopherol or a mixture of natural tocopherols. In a preferred embodiment γ -tocopherol is used.

30

The lecithin, ascorbyl palmitate and tocopherol are preferably used in a ratio of 6-3:4-2:8-4, especially 3:2:4, and the combined amount thereof incorporated into the silica-treated oil is preferably 1000-4000 parts per million, especially 2000-3500, preferably ca. 3000 parts per million. The lecithin, ascorbyl palmitate and tocopherol can be incorporated as a mixture or individually. When a mixture is used, the incorporation is preferably carried out at about

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20-90°C, especially about 60°C. When the components are incorporated individually, the lecithin is preferably incorporated at above about 40°C, especially at about 60°C, the ascorbyl palmitate is preferably incorporated at above about 90°C, especially at about
5 130°C, and the tocopherol is preferably incorporated at above about 20-60°C, especially at about 60°C.

An oil which is even superior in taste and smell can be obtained when an additional so-called soft vacuum steam deodorization,
10 preferably at a temperature between about 140°C and about 210°C is carried out before the lecithin, ascorbyl palmitate and tocopherol are incorporated in the silica-treated oil. This additional step can be carried out using conventional equipment and in a batch, semi-batch
15 between about 150°C and about 170°C, or even about 190°C for about 2 to about 5 hours, especially about 1 to about 4 hours, under a pressure of about 2 to about 10 mbar, especially about 3 to about 5 mbar.

20 The term "soft" should indicate that this deodorisation step is carried out at temperatures which are (somewhat) lower than the usual deodorization temperatures, and/or at reaction times which are (somewhat) shorter than the usual reaction times used in this process.

25 The use of the aforementioned steam deodorization permits a reduction in adsorbent levels from 50-20% by weight (adsorbent/oil) to as low as 5%, which is more attractive economically. The latter figure would in fact be 1/4 of the amount used (i.e. 20%) without this additional step.

30

The stabilized marine oils manufactured in accordance with the invention are useful for incorporation into foodstuffs such as margarines, spreads, mayonnaise and the like and into cosmetic and dietary products, e.g. supplements.

35

The following Examples illustrate the present invention, but do not limit the scope thereof in any manner. In the Examples the lecithin used was Epikuron 100G.

5

Example 1

(a) 100 g of conventionally degummed, neutralized and bleached marine oil containing 18% EPA and 12% DHA were mixed with 50 g of wet Trisyl (60% water content) and heated to 80°C while stirring
10 vigorously under a vacuum, which rapidly reached 70 mbar and gradually increased to 25 mbar over a period of 1 hour when bubbles ceased to evolve from the mixture. The heating was stopped, the vacuum was broken, the mixture was cooled to 40°C and 200 g of hexane were added. The mixture was filtered over a funnel (9 cm
15 diameter; Whatman No. 1 paper during 5 minutes, the filter residue comprising a silica bed was washed with 40 g of hexane and the combined filtrate and washings were evaporated, initially under a low vacuum and then under a high vacuum (1 mbar for 1 hour). There were obtained 94.5 g of a pale yellow odour-free oil having a mild
20 fish taste.

(b) A mixture of lecithin, ascorbyl palmitate and γ -tocopherol in an amount of 750:500:1000 ppm was dissolved in the oil obtained according to (a) by heating at 90°C for 1 hour on a rotary evaporator
25 (25 mbar vacuum) to give the desired stabilized oil.

(c) The oil obtained according to (b) was evaluated for stability on a Rancimat® apparatus (Metrohm Ltd., CH-9101 Herisau, Switzerland) at 100°C. The oil showed an induction time (i.e. the time taken for the oil
30 to reach the onset of rancidity) of 10.1 hours compared with an induction time of 1.5 hours for the oil obtained according to (a).

Example 2

35 The procedure described in Example 1 was repeated except that a mixture of lecithin, ascorbyl palmitate and α -tocopherol was used in (b) in an amount of 750:500:1000 ppm. The induction time of the

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thus-stabilized oil determined on a Rancimat® apparatus at 100°C was 7.1 hours.

Example 3

5

The procedure described in Example 1 was repeated except that in (a) the hexane treatment was omitted and the mixture was filtered directly to give 83 g of a pale yellow odour-free oil having a mild fish taste and in (b) a mixture of lecithin, ascorbyl palmitate and α -
10 tocopherol was used in an amount of 750:500:1000 ppm.

Evaluation of the resulting stabilized oil on a Rancimat® apparatus gave an induction time of 8 hours at 100°C.

15

Example 4

(a) 100 g of conventionally degummed, neutralized and bleached marine oil containing 18% EPA and 12% DHA were dissolved in 200 g of hexane and 20 g of dry chromatographic grade silica were added.
20 The mixture was stirred for 5 minutes and then filtered. over a No. 2 porosity sintered filter at a flow rate of 1ml/cm²/minute. After washing the silica present on the filter with 40 g of hexane and the combined miscella and washings were evaporated to give 91.4 g of a taste-free and odour-free pale yellow oil.

25

(b) A mixture of lecithin, ascorbyl palmitate and γ -tocopherol in an amount of 750:500:1000 ppm was dissolved in the oil obtained according to (a) by heating at 90°C for 1 hour on a rotary evaporator (25 mbar vacuum) to give the desired stabilized oil.

30

(c) The stability of the oil obtained according to (b) was evaluated on a Rancimat® apparatus at 90°C. The oil showed an induction time of 27.7 hours compared with an induction time of 1.5 hours for the oil obtained according to (a).

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Example 5

150 g of deodorized marine oil were mixed with 30 g of silica (GRACE Trisyl SP 2-7887) and the mixture was heated to 80°C for 2 hours at about 30 mbar on a rotary evaporator. The suspension was then cooled to room temperature and 300 g of hexane were added. The mixture was stirred for 1.5 hours and filtered. The hexane was removed from the mixture on a rotary evaporator to yield 146.6 g of a clear yellow oil with a slightly fishy taste and smell.

10

140 ml of this oil were "soft" deodorized at 155 °C under 5 mbar for 2.5 hours and then cooled to room temperature. The deodorized oil was free from the taste and smell of fish. 750 ppm of lecithin, 1000 ppm of α -tocopherol and 500 ppm of ascorbyl palmitate were added at 60°C.

15

The Rancimat induction time (100°C, 20 l air/hour) recorded for this oil was 9.25 hours compared with 6.4 hours for the silica-treated oil without the soft deodorization step, but stabilized in the same manner.

20

Example 6

200 g of deodorized marine oil were mixed with 40 g of silica (GRACE Trisyl SP 2-7915) and the mixture was heated to 80°C for 2 hours at about 30 mbar on a rotary evaporator. The suspension was then cooled to room temperature and 400 g of hexane were added. The mixture was stirred for 1.5 hours and filtered. The hexane was removed from the mixture on a rotary evaporator to yield 165.2 g of a clear yellow oil with a slightly fishy taste and smell.

30

127 ml of this oil were "soft" deodorized at 155 °C under 5 mbar for 2.5 hours and then cooled to room temperature. The deodorized oil was free from the taste and smell of fish. 750 ppm of lecithin, 1000 ppm of α -tocopherol and 500 ppm of ascorbyl palmitate were added at 60°C.

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The Rancimat induction time (100°C, 20 l air/hour) recorded for this oil was 4.9 hours compared with 3.4 hours for the silica treated oil stabilized in the same manner.

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Example 7

200 g of deodorized marine oil were mixed with 40 g of silica (GRACE Trisyl SP 2-7915) and the mixture was heated to 80°C for 2 hours at about 30 mbar on a rotary evaporator. The suspension
10 was then cooled to room temperature within 1.5 hours and filtered to yield 165. g of a clear yellow oil with a slightly fishy taste and smell.

125 ml of this oil were "soft" deodorized at 155 °C under 5 mbar for 2.5 hours and then cooled to room temperature. The
15 deodorized oil was free from the taste and smell of fish. 750 ppm of lecithin, 1000 ppm of α -tocopherol and 500 ppm of ascorbyl palmitate were added at 60°C.

The Rancimat induction time (100°C, 20 l air/hour) recorded for
20 this oil was 5.2 hours compared with 4.5 hours for the silica treated oil without the soft deodorization step, but stabilized in the same manner.

Example 8

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1.582 g of deodorized marine oil were mixed with 79 g of silica (GRACE Trisyl SP 2-8998) and the mixture was heated to 80°C for 2 hours at about 30 mbar on a rotary evaporator. 31.6 g of activated carbon (Norit CA1) were added and the mixture was heated for a
30 further hour under a vacuum of 30 mbar. After cooling, the mixture was filtered to yield a clear yellow oil with an unpleasant taste and smell; neither of which could be described as fishy.

500 ml of this oil were "soft" deodorized at 190°C for 2 hours at
35 4 mbar and then cooled to room temperature. The deodorized oil was free from the taste and smell of fish. 750 ppm of lecithin, 1000 ppm of α -tocopherol and 500 ppm of ascorbyl palmitate were added at 60°C.

The Rancimat induction time (90°C; 20 l air/hour) recorded for this oil was 11 hours, compared with 7 hours for the oil prior to the final deodorization and 0.5 hour for the oil used as the starting
5 material.

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Claims:

1. A process for the stabilization of fully or partially refined marine oil, which process comprises treating said oil with silica and incorporating a lecithin, ascorbyl palmitate and a tocopherol in the thus-treated oil.
2. A process according to claim 1, wherein fully refined marine oil is used.
3. A process according to claim 1 or claim 2, wherein the silica is dried or substantially freed from water before or during the process.
4. A process according to any one of claims 1 to 3, wherein a silica having a surface area greater than 500 m² per gram is used.
5. A process according to any one of claims 1 to 4, wherein the silica treatment is carried out by contacting the oil with the silica in a column or stirred reactor vessel or a combination thereof.
6. A process according to any one of claims 1 to 5, wherein the silica treatment is carried out by passing an oil/solvent miscella through silica in a column or stirred reactor vessel or a combination thereof, filtering and subsequently removing the solvent.
7. A process according to claim 6, wherein the solvent is a food grade approved apolar solvent.
8. A process according to claim 7, wherein said solvent is a hydrocarbon.
9. A process according to claim 8, wherein said hydrocarbon is hexane.
10. A process according to any one of claims 1 to 9, wherein the treatment with silica is carried out in the presence of carbon.

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11. A process according to claim 10, wherein the carbon is dried or substantially freed from water before or during the process.

12. A process according to claim 10 or claim 11, wherein a
5 carbon having a surface area greater than 1100 m² per gram is used.

13. A process according to any one of claims 1 to 12, wherein the lecithin, ascorbyl palmitate and tocopherol are used in a ratio of 6-3:4-2:8-4.

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14. A process according to claim 13, wherein the ratio is 3:2:4.

15. A process according to any one of claims 1 to 14, wherein the combined amount of lecithin, ascorbyl palmitate and tocopherol
15 incorporated in the silica-treated oil is 1000-4000 parts per million.

16. A process according to claim 15, wherein the combined amount is 2250 parts per million.

20 17. A process according to any one of claims 1 to 16, wherein the lecithin, ascorbyl palmitate and tocopherol are incorporated as a mixture.

25 18. A process according to claim 17, wherein the incorporation is carried out at about 20-90°C.

19. A process according to claim 18, wherein the incorporation is carried out at about 60°C.

30 20. A process according to any one of claims 1 to 16, wherein the lecithin, ascorbyl palmitate and tocopherol are incorporated separately.

35 21. A process according to claim 20, wherein the lecithin is incorporated at above about 40°C.

22. A process according to claim 21, wherein the lecithin is incorporated at about 60°C.

23. A process according to any one of claims 20 to 22, wherein the ascorbyl palmitate is incorporated at above about 90°C.

5 24. A process according to claims 23, wherein the ascorbyl palmitate is incorporated at about 130°C.

25. A process according to any one of claims 20 to 24, wherein the tocopherol is incorporated at about 20-60°C.

10

26. A process according to claim 25, wherein the tocopherol is incorporated at about 60°C.

15 27. A process according to any one of claims 1 to 26, wherein the silica-treated oil is subjected to a soft vacuum steam deodorization at a temperature between about 140°C and about 210°C prior to the incorporation of the lecithin, ascorbyl palmitate and tocopherol.

28. A process according to claim 27, wherein the temperature
20 is about 150°C to about 170°C.

29. A process according to claim 27 or claim 28, wherein the deodorization is carried out for about 1 to about 5 hours.

25 30. A process according to claim 29, wherein the deodorization is carried out for about 1 to about 4 hours.

31. A process according to any one of claims 27 to 30, wherein the pressure is about 2 to about 10 mbar.

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32. A process according to claim 31, wherein the pressure is about 3 to about 5 mbar.

33. A marine oil stabilized according to the process claimed in
35 any one of claims 1 to 32.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 92/02543

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C11B5/00; C11B3/10; A23D9/00; C09K15/06

II. FIELDS SEARCHEDMinimum Documentation Searched⁷

Classification System

Classification Symbols

Int.Cl. 5

C11B ;

A23D ;

C09K

Documentation Searched other than Minimum Documentation
to the extent that such Documents are included in the Fields Searched⁸**III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹**

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	EP,A,0 340 635 (KABIVITRUM AB) 8 November 1989 see page 5, line 36 - line 54 see page 13; table 2 see claims 1-8 ---	1-33
Y	EP,A,0 326 829 (SOCIETE DES PRODUITS NESTLE) 9 August 1989 see page 1, line 1 - line 16; example 7 ---	1-33
Y	US,A,5 006 281 (DAVID RUBIN ET AL.) 9 April 1991 see column 4, line 54 - line 64 see column 5, line 55 - column 6, line 3 see column 7, line 38 - column 8, line 10; example 2 --- -/--	1-33

¹⁰ Special categories of cited documents:

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IV. CERTIFICATION

Date of the Actual Completion of the International Search

14 JANUARY 1993

Date of Mailing of this International Search Report

10.02.93

International Searching Authority

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Signature of Authorized Officer

DEKEIREL M.J.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		Relevant to Claim No.
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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

EP 9202543
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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